J. nat. Rubb. Res., **1(3)**, 202–208

Storage Hardening of Natural Rubber: An Examination of Current Mechanistic Proposals

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The paper reviews the evidence for the presence of reactive functional groups in natural rubber and critically examines the mechanisms proposed to account for the storage hardening phenomenon. The review recognises the complexity of the natural rubber system and suggests that current proposals are as yet inadequate to explain all the observed characteristics of storage hardening. It is speculated that the prominent effect of humidity may be best accounted for by the formation of ionic crosslinks the strength of which are determined by the level of hydration of the ionic species.

The progressive hardening that occurs in natural rubber on prolonged storage under ambient conditions has been known for several decades; but the mechanism by which this process occurs has yet to be unequivocally established. Over the years, certain characteristics of the process have however been clearly identified and these include the following:

- the process is markedly accelerated by conditions of low humidity[1] and this had led to the development of an accelerated storage hardening test (ASHT)[2,3,4].
- various reagents, notably amines such as hydroylamine, inhibit the hardening process if added to the latex before isolation of the rubber in sufficient quantity[5,6].
- the process is catalysed by the presence of amino-acids in the latex[7].

The above features are however, capable of a variety of explanations and this has led authors to variously implicate carbonyl[5,7-9] (most probably aldehyde), lactone[10] and epoxide[11-14] groups as the major culprit in the process.

Distinguishing between the various proposals is not a simple task due to the complexity of the natural rubber system and the low levels of abnormal groups which are believed to be operative in the crosslinking reaction. One possible approach is to seek to identify the functional groups present in the rubber. Establishment of the presence of a particular group while a necessary condition is not in itself a sufficient one, since the group though present may not be involved in crosslinking. A second approach therefore is necessary. This involves demonstrating that a plausible reaction scheme exists which takes into account the known features of the storage hardening process.

Conversely, a proposal may be discounted if it is shown that the hypothesised crosslinking reaction is inconsistent with experimental observations. A recent publication[15] has taken this latter approach and purports to show that proposals involving epoxide groups are irreconcilable with model studies involving epoxidised rubbers. This paper examines the validity of that claim and concurrently briefly reviews the evidence for the presence of reactive functional groups in natural rubber and examines related crosslinking proposals.

DISCUSSION

Evidence for Natural Rubber Functionality

The presence of carbonyl groups, most probably aldehydic in nature, was originally inferred largely on the basis of circumstantial evidence. Thus it was observed that amines and more particularly aldehydic reagents such as

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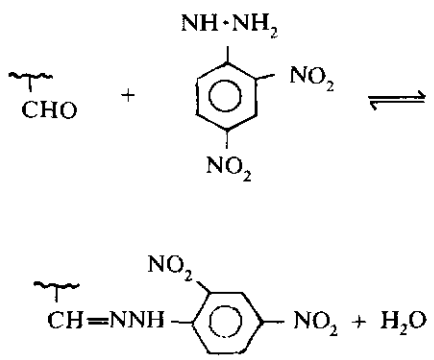
dimedone[16] were effective inhibitors of the hardening process. It was suggested that the most plausible explanation indicated the presence of aldehyde groups. More direct evidence for carbonyl groups was provided by the careful work of Subramaniam[9,17] who estimated the concentration of such groups by reaction with dinitrophenylhydrazine (DNPH), *Equation 1:*



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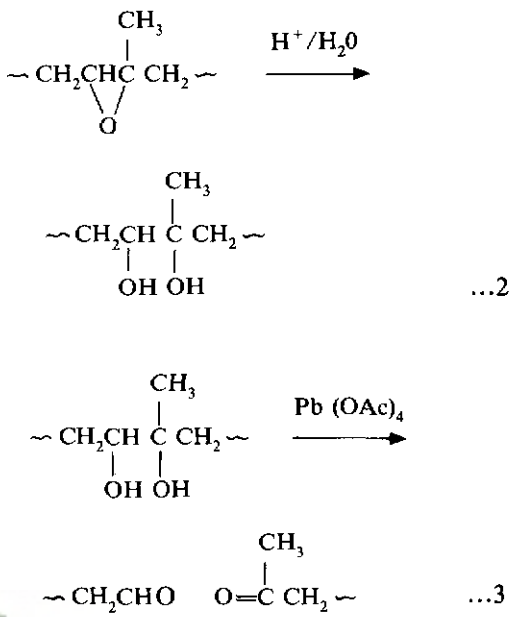
followed by determination of the resultant rubber hydrazone content by UV.

Subsequent evaluation of the specificity of the DNPH method[18] showed that under suitable conditions aldehyde groups are quantitatively assayed, whereas ketonic groups are less reactive and other groups such as epoxide, ester or carboxyl do not interfere in the analysis. Examination[18] of rubbers from freshly-tapped latices confirmed the formation of a DNPH derivative at a level of about 5×10^{-6} mol per gramme. The observed λ_{max} value of the rubber DNPH derivative of, *ca.*, 353–355 nm suggests the presence of a non-conjugated aldehyde. Further confirmatory evidence for the presence of rubber aldehyde groups was provided by the work of Percy (described in an appendix to reference 17) who showed that ^{14}C-labelled dimedone was incorporated into rubber again at levels approaching 5×10^{-6} mol per gramme. These reports[9,17,18] probably thus represent the best evidence for naturally occurring aldehyde groups since direct determination by NMR has yet to be accomplished.

The presence of epoxide groups was initially postulated[11] on the basis of the observed reduction in molecular weight accompanying the lead tetracetate induced degradation of acid hydrolysed rubbers. The chain scission was attributed to the following reaction sequences:



Later more detailed studies[19] which included various controls and model polymer systems and employed periodic acid as an alternative chain scission reagent confirmed the validity of the original speculations. A close examination of these results leaves little doubt that natural rubber, after acid hydrolysis, contains weak links which are rapidly cleaved by treatment with reagents regarded as specific for 1,2-diols and related compounds. The most plausible explanation still appears to be the presence of main-chain epoxide groups or their derivatives.

Subsequently[12], it was shown that the concentration of epoxide and amine groups present in natural rubber could be determined by a direct titration method with HBr. A careful examination of the specificity of the method with respect to functional groups likely to be present in the rubber showed that, under the

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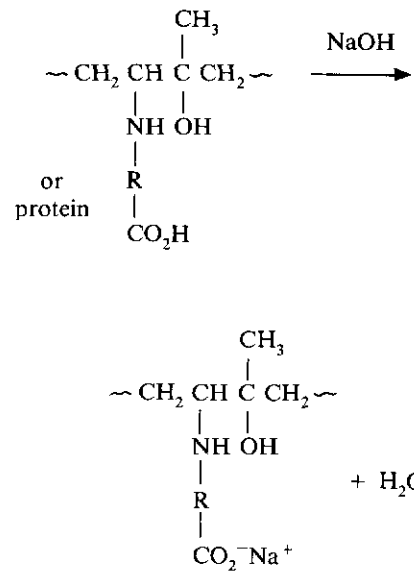
titration conditions employed, epoxide and amine groups were quantitatively determined and that no interferences were likely. It was also shown that by applying an ingenious double titration technique the epoxide and amine entities could be distinguished. Both groups were found to occur in natural rubber samples with clonal variation of epoxide groups in the approximate range 45×10^{-6} mol to 75×10^{-6} mol per gramme. An examination[13] of the distribution of these groups showed a predominance in the higher molecular weight fractions thus demonstrating that epoxides are not an artifact of oxidative degradation.

More recently[20], elegant NMR studies of highly purified natural rubbers reveal the presence of low levels of epoxide groups in rubbers derived from commercial latices. Epoxy contents between 15×10^{-6} mol and 20×10^{-6} mol per gramme have been estimated by both ^{1}H and ^{13}C-NMR measurements. These direct observations are important since they confirm the presence of main-chain isoprenic epoxides. It should be noted however that the latest studies are less supportive in that significant concentrations of epoxide have yet to be detected in highly purified rubbers from freshly-tapped latices. It is perhaps tempting to suspect that the epoxy content of commercial latices may be derived from oxidative ageing of the latex, however the failure to observe aldehydic groups, a usual oxidation product, weakens this argument. It may be relevant that the epoxide groups are concentrated in the higher molecular weight or gel fraction and these may not be well represented in the highly purified rubbers obtained from fresh latices.

The proposal[10] that natural rubber is essentially a high molecular weight lactone is based on a series of IR observations of purified and chemically treated rubbers. Thus base hydrolysis of the gel fraction led to the detection of carbonyl stretching frequencies attributable to a carboxylic acid salt, whereas acid hydrolysis led to the detection of a cyclic ester (lactone) structure. However, as has already been pointed out these observations are consistent with the presence of epoxide-derived groups *(vide infra)*. Thus base hydrolysis will promote reactions such as:



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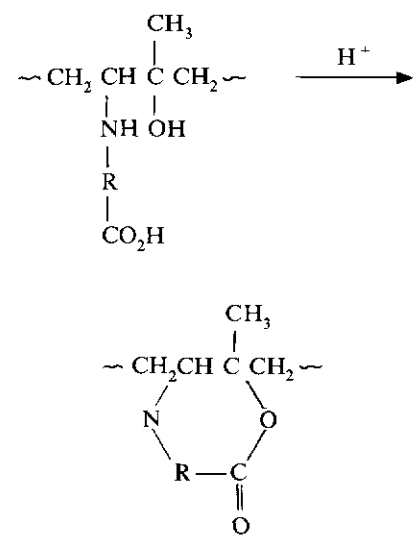
whereas, acid hydrolysis will lead to ring closure, e.g.:



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and hence observation of a cyclic ester.

In summary, the evidence suggests that natural rubber contains both epoxide and aldehydic groups, the latter at very low levels, and that lactone groups may be derived indirectly from the epoxide entity.

Proposed Mechanisms for Storage Hardening

It is generally agreed that the hardening of rubber is due to inter-chain crosslink formation which is not free radical or oxidative in nature. This is particularly inferred from the determining influence of humidity and the relative unimportance of anaerobic conditions to the process. The proposed mechanisms centre around the reactions of the functional groups believed responsible for the crosslinking and these are discussed below.

Aldehydic crosslinking. The initial proposal attributing crosslink formation to aldehyde groups was not specific as to the actual mechanism involved. However, on the basis of inhibition by added aldehydes, it was suggested[8] that the rubber also contained 'aldehyde condensing groups' which could react with the rubber aldehydes. The nature of these groups was not determined although it was speculated that α-methyl or methylene groups could be involved.

Later, it was suggested[2] that crosslinking occurred by a bimolecular aldol condensation between rubber aldehyde groups but no details were given. This proposal was outlined in more detail by Gorton[21] who however used it to rationalise viscosity increases in *latex* storage. The proposal was based on the following reactions:

$$(NR)-CH_2CHO + OHC\,CH_2-(NR) \overset{OH^-}{\rightleftharpoons} (NR)-CH_2CH(OH)\,CH(CHO)-(NR) \quad \ldots 6$$

$$\downarrow$$

$$(NR)-CH_2CH=C(CHO)-(NR) + H_2O \quad \ldots 7$$

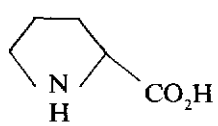
where, the condensation was promoted by the high pH of the stored latices.

In order to account for the catalysis by amino-acids Gregory and Tan[7] proposed a modified mechanism which may be represented as follows:

$$R\,CH_2\,CHO + R'NH_2 \rightleftharpoons R\,CH_2\,CH=NR' + H_2O \quad \ldots 8$$

$$R\,CH_2\,CH=NR' + R\,CH_2CHO \longrightarrow R\,CH_2\,CH(RCHCHO^{\cdot})\,NHR' \quad \ldots 9$$

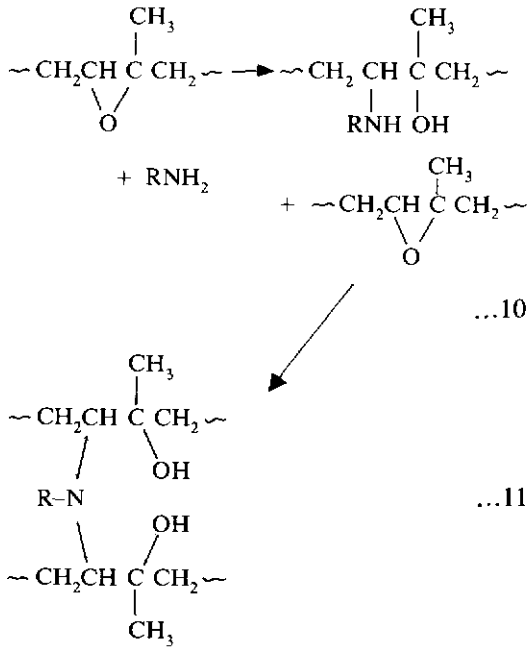
where $R'NH_2$ represents the conjugate base of an amino acid. This proposal however appears inadequate to accommodate all their observations since the cyclic amino acid proline



which accelerates storage hardening could not be involved in imine formation as required by *Equation 8.*

It is clear from an examination of the above proposals that a major discrepancy exists between the characteristics of the mechanism and the experimental observations of storage hardening. This is highlighted by the fact that essentially the same mechanism is postulated to account for crosslink formation in latex[21] and in *dry* rubber[2,7] even though storage hardening is known to be greatly accelerated and increased by essentially anhydrous conditions. Despite the elimination of water in the second stage of the condensation *(Equation 7)* both aldol type condensations and aldehyde-amine reactions are efficiently carried out in aqueous media[22]. It should be further noted that crosslinks will effectively form whether or not the reaction goes to the second stage of dehydration *(Equation 7).*

Epoxide crosslinking. The original proposal[11] suggested that rubber epoxide groups could be crosslinked by amino compounds derived from the latex. Reactions such as:



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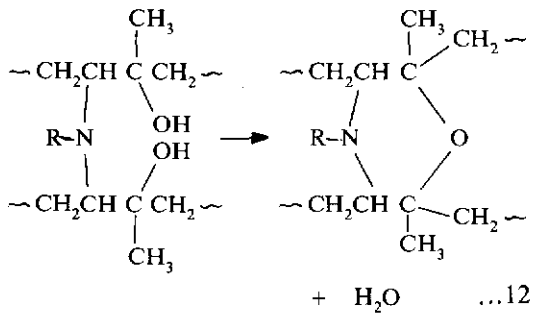
were envisaged to occur in latex, followed by dehydration under low humidity conditions in the dry rubber:



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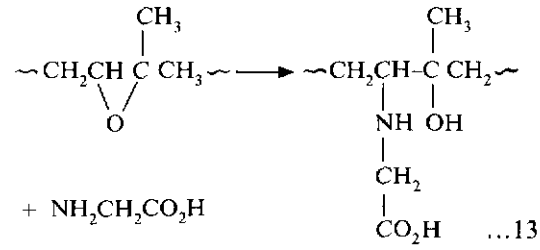
An apparent weakness of the proposal was the low reactivity of rubber epoxides towards amino compounds — even at elevated temperatures[23]. However, it was subsequently demonstrated, with model compounds, that the presence of water[24] or β-substituted hydroxyl group[25] activated the ring-opening reactions to the extent that the reactions occurred smoothly at ambient temperatures. Thus epoxide ring-opening reactions are to be anticipated in latex medium.

This mechanism however shares the same drawback as the aldehydic proposals since it cannot readily account for the importance of low humidity conditions. Thus, the ring closure reaction *(Equation 12)*, although feasible, is unlikely to subtantially increase the *effective* number of crosslinks. Because of this deficiency and in order to take into account the demonstrable effect of amino acids[7], a revised mechanism was put forward[12]. It was suggested that epoxide groups were ring opened by amino acids at the latex stage to give a functionalised rubber:



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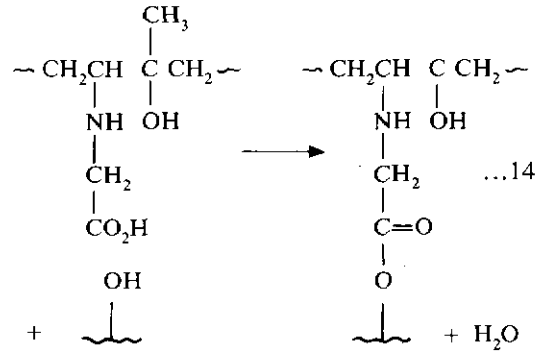
and that crosslinks were subsequently formed under low humidity conditions by reactions such as:



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Evidence for *Reaction 13* was provided by radio-tracer studies which showed that labelled glycine added to fresh latices was incorporated into the rubber at levels close to the known epoxy content[14].

Recently, Subramaniam and Wong[15] published model studies relating to the above proposals. In their studies the relevance of

epoxide groups to storage hardening has been evaluated by the addition of glycine to epoxidised synthetic and purified natural rubber controls. The results show that the synthetic model does not storage harden but that the epoxidised natural rubber control underwent the usual hardening described in earlier reports[7]. The authors conclude that since the presence of epoxide groups does not enhance storage hardening the proposed epoxide mechanism must be incorrect.

These results are important as they help to further clarify the nature of the crosslinking process, however, they do not necessarily preclude the involvement of epoxide groups. It is already clear from earlier model studies[23,24,25] that tri-substituted epoxide groups are relatively unreactive to nucleophilic attack by amino compounds under non-aqueous conditions. Furthermore, recent reports[26] show that even the more favourable electrophilic addition of carboxylic acids require reaction temperatures of around 160°C. It is therefore not surprising that dry epoxidised rubbers should remain inert to glycine at 60°C. This finding however in no way rules out similar reactions in the latex phase which is the basis of the revised mechanism[12,14] discussed above. It should be noted at this juncture that it is believed that rubber epoxide groups result from an enzymic epoxidation process[13] and it is conceivable that further reactions of these groups may be bio-assisted.

One difficulty remains; if amino acids only react with epoxide groups in latex how do these entities promote storage hardening in dry rubber as reported in the recent publication[15]. The simplest explanation is that the glycine acts as a catalyst to promote the esterification reactions proposed to occur in dry rubber *(Equation 14)*. This would be a somewhat similar role to that suggested for amino-acids under the aldehydic mechanism. An alternative possibility is outlined below.

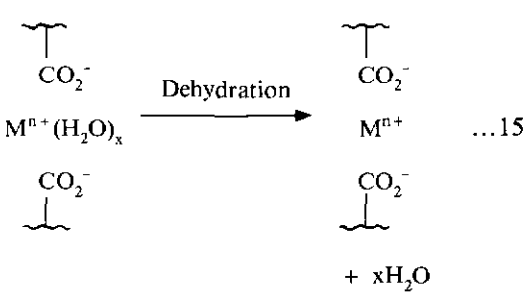
Lactone crosslinking. Gregg and Macey[10] suggested that natural rubber forms as a prosthetic group connected through a lactone linkage to a protein molecule in the cell of *Hevea brasiliensis*. The tendency of rubber to gel is considered to be due to inter-chain lactone interchange or interaction with denatured protein. However, no clear explanation of the crosslinking mechanism was formulated. It is thus difficult to comment on those proposals other than to point out that the lactone groups may in fact be derived from epoxide precursors *(vide supra)*.

SUMMARY

It is readily apparent that storage hardening is a complex process, the mechanism of which has yet to be firmly elucidated. Thus it is entirely conceivable that more than one type of mechanism may be operative and this may give rise to apparent conflicting conclusions by different authors. Thus the process which gives rise to hardening and gel formation on latex storage may well be quite different from that occurring in dry rubbers. Similarly, the mechanism of hardening in whole latex films may show important differences compared to sheet rubbers obtained by acid coagulation, where the non-rubber components are much reduced in concentration.

A key characteristic of rubber hardening is the sensitivity to moisture which in the author's opinion is not adequately accounted for in the current mechanisms. A possible alternative is some type of ionic crosslink mediated by metal ions or amino acid zwitter ions. Such systems are known to be sensitive to moisture, for example, the tensile strength of CaO cross-linked carboxylated rubbers is dramatically reduced under conditions of high humidity[27].

Ionic crosslinks could be envisaged to form with the epoxide bound amino acids *(Equation 13)*, and could be represented as:



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The sensitivity to moisture is explicable since strongly hydrated ions reduce the strength of

the link. Conversely, drying the rubber reduces the solvation by water, intensifies the ionic interactions and hence effectively increases the crosslink density. Work is currently in hand to further probe this suggested mechanistic alternative.

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